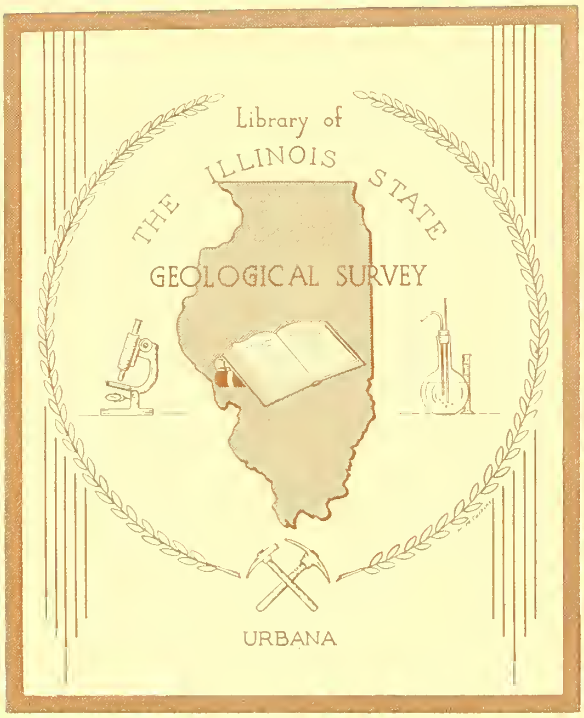

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ENVIRONMENTAL GEOLOGY NOTES

SEPTEMBER 1970 • NUMBER 37

STUDIES OF LAKE MICHIGAN BOTTOM SEDIMENTS—NUMBER FOUR

DISTRIBUTION OF ARSENIC IN UNCONSOLIDATED SEDIMENTS FROM SOUTHERN LAKE MICHIGAN

R. R. Ruch, E. Joyce Kennedy, and Neil F. Shimp

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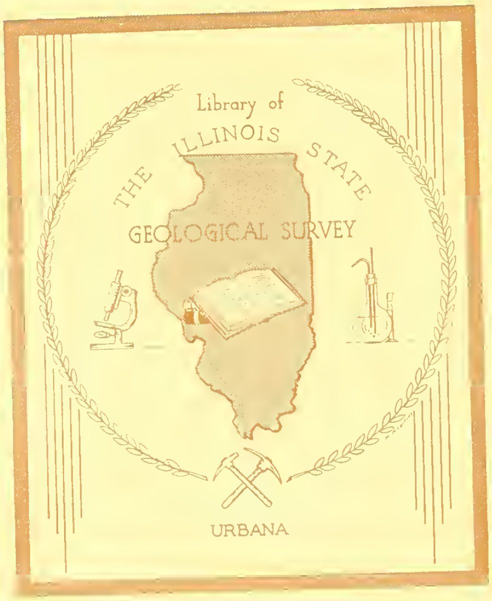

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ABSTRACT

Radiochemical separation procedures were used to determine the arsenic content of 89 core and grab samples from southern Lake Michigan. Arsenic was found to accumulate within the upper, or most recently deposited, portion of most of these sediments in concentrations ranging from about 5 to 30 ppm. Areas with high arsenic content were identified from sediment-water interface samples taken west of Benton Harbor, Michigan; east of Waukegan, Illinois; and southwest of Grand Haven, Michigan. Deposition of fine-grained sediments containing appreciable quantities of organic matter occurs at all these locations. Amounts of arsenic observed in the uppermost portions of these sediments generally vary directly with the organic carbon content and are probably a result of man's activities in the watershed surrounding the lake.

INTRODUCTION

This is the fourth in a series of reports covering investigations of the geology and chemical composition of Lake Michigan sediments. Like the previous three (Gross et al., 1970; Shimp, Leland, and White, 1970; and Lineback, Ayer, and Gross, 1970), it is part of a comprehensive study conducted by the Illinois State Geological Survey and the University of Illinois. Selection of sampling locations and acquisition of cores for chemical analysis were made by Dr. H. V. Leland of the University's Civil Engineering Department.

Major chemical objectives of these investigations are to assemble data on the distribution of trace elements in Lake Michigan sediments and to determine which geochemical processes operating during sedimentation affect the distribution of trace elements. Initial chemical results were reported by Shimp, Leland, and White (1970).

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This report deals specifically with the distribution of arsenic in sediments of southern Lake Michigan. The toxicity of arsenic is well known, and responsible use and disposal of this chemical is of major concern to scientific and environmental agencies. The possibility of pollution due to indiscriminate use of pesticides containing arsenic has long been recognized (Spencer, 1970). Fears of environmentalists have been intensified by reports of possible arsenic pollution from the use of detergents (Angino et al., 1970). Recently, an accumulation of arsenic was found in manganese nodules taken from the Green Bay area of Lake Michigan (Edgington and Callender, 1970). The amounts of arsenic present in the sediments of Lake Michigan, however, have not been previously reported.

METHODS

The techniques, gear, and procedures used for obtaining the core and grab samples used in this investigation were described in detail by Gross et al. (1970) and Shimp, Leland, and White (1970). The methods for determination of organic carbon and less than 2-micron clay also were described in the latter report.

Radiochemical Determination of Arsenic

From 0.7 to 1.0 g of oven-dried (110° C) sediment was accurately weighed and placed in a 2 cc polyethylene snap-cap vial. The samples were irradiated in the University of Illinois TRIGA MK II nuclear reactor for half an hour in a thermal neutron flux of 5×10^{12} neutrons cm^{-2} sec^{-1} to convert the arsenic to radioactive arsenic-76 (^{76}As). A comparative standard containing 95.6 μ g of arsenic was irradiated with the samples in a rotating device (1 rpm) that assured equal neutron flux for standard and samples. Radiation doses were 100 to 200 mr per sample following irradiation. After decaying overnight, each sample was quantitatively transferred to a platinum crucible and treated as follows.

A nonradioactive arsenic carrier (32 mg of As^{+5}) was added to help insure isotopic exchange and known recovery of ^{76}As from the sample during subsequent chemical separation. One ml of 30 percent hydrogen peroxide solution, 1 ml of concentrated perchloric acid, and 10 to 15 ml of concentrated hydrofluoric acid were then added. The mixture was heated at about 100° C for about 8 hours until the silica in the sediment had been volatilized. Another 0.5 ml of perchloric acid was added, and the crucible was covered and heated at 200° to 250° C until a clear solution was obtained. The sample was never allowed to evaporate to dryness. Approximately 7 ml of concentrated hydrochloric acid was added and the sample was transferred to a distillation flask. Fifteen ml of concentrated hydrobromic acid was added and the solution was distilled in an air stream until about 20 ml of distillate was collected in a flask containing 30 ml of deionized water. A second 15 ml of hydrobromic acid was added and distillation was repeated. The combined distillate was checked for clarity and filtered if necessary. Approximately 5 g of sodium hypophosphite was then added and the mixture warmed to 80° to 90° C for about 3 hours, until reduction to arsenic metal was complete.

The arsenic standard was quantitatively transferred to a distillation flask containing 32 mg of nonradioactive As^{+5}, 5 ml of concentrated hydrochloric

acid, and 15 ml of concentrated hydrobromic acid and distilled in the same manner as the samples.

Arsenic metal precipitates were filtered onto a preweighed filter paper 1-inch in diameter, washed with deionized water, dried with acetone, weighed, and mounted onto cardboard for gamma ray counting.

The 0.56 Mev gamma ray photopeak of ^{76}As was used for quantitatively estimating arsenic in the sediment samples. Counting was performed at a close geometry above a 3 x 3-inch sodium iodide detector connected to a RIDL 34-27 multichannel analyzer system. The radiochemical purity of all samples processed was excellent, with chemical yields consistently above 70 percent. The over-all precision of this technique is estimated to be ± 7 percent. The U. S. Geological Survey rock standard W-1 was analyzed by this procedure and a value of 2.3 ± 0.2 ppm arsenic was obtained. The accepted standard value is 2.4 ppm (Fleischer, 1969).

RESULTS AND DISCUSSION

Complete descriptions of the Lake Michigan core and grab samples are given in Gross et al. (1970), Shimp, Leland, and White (1970), Lineback, Ayer, and Gross (1970). Figure 1 shows the location of the sampling stations from which the samples analyzed in this report were taken. Table 1 indicates the type of sample taken at these stations.

TABLE 1—TYPE OF SAMPLE AND LOCATION OF SAMPLING STATIONS

Station	Type of sample	Depth of water (ft)	Latitude	Longitude
11	3-in. diam. core	203	41°58.9'N	87°06.7'W
44	3-in. diam. core	238	42°21.8'N	87°34.5'W
51	3-in. diam. core	440	42°49.9'N	86°50.5'W
65	Grab sample	150	41°55.5'N	86°58.1'W
72	Grab sample	78	41°45.5'N	87°10.5'W
75	Grab sample	105	41°52.2'N	87°15.5'W
101	3-in. diam. core	250	42°59.2'N	86°25.9'W
105	3-in. diam. core	186	42°13.8'N	86°37.0'W
110	3-in. diam. core	102	42°08.0'N	86°36.5'W
113	3-in. diam. core	230	42°09.0'N	86°43.8'W
115	3-in. diam. core	276	42°09.8'N	86°48.1'W
118	3-in. diam. core	312	42°08.0'N	86°36.5'W
124	3-in. diam. core	233	42°02.0'N	86°57.0'W
140	3-in. diam. core	200	42°06.8'N	87°21.4'W
141	3-in. diam. core	252	42°11.6'N	87°18.0'W
142	3-in. diam. core	300	42°16.2'N	87°14.8'W
145	2-in. diam. core	346	42°21.8'N	87°20.3'W
148*	2-in. diam. core	240	42°21.8'N	87°34.5'W
150	3-in. diam. core	520	42°34.2'N	86°57.1'W

* Core 148 is a deeper extension of core 44.

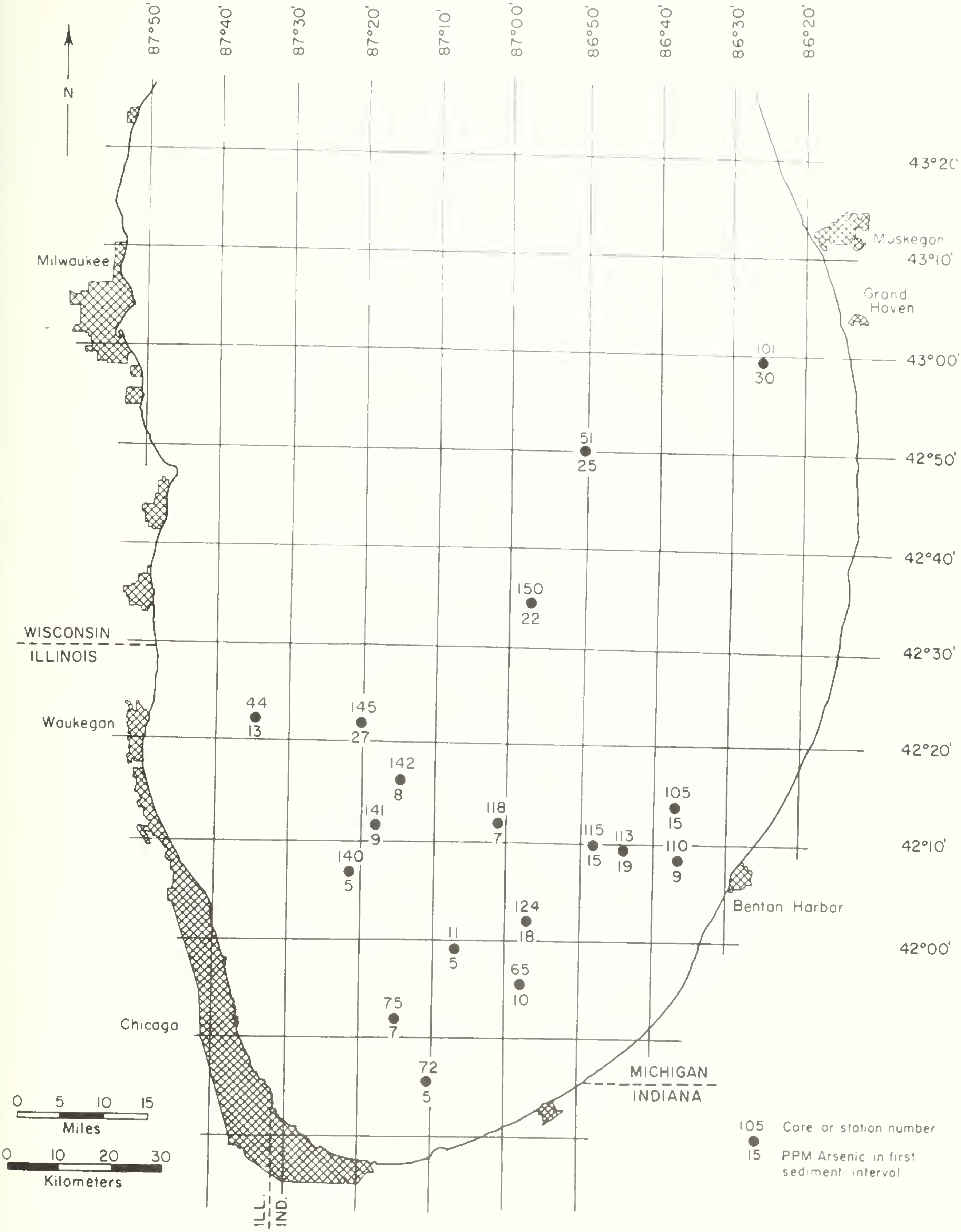


Fig. 1 - Sample locations and arsenic content for the uppermost sediment interval.

Arsenic, organic carbon, and less than 2-micron clay concentrations obtained for each core or grab sample are given in table 2 and plotted against depth in figures 2 through 17. In general, the upper or most recently deposited sediments have the highest arsenic concentrations. Wherever such accumulation occurs, the amount of arsenic is more closely related to variations in organic carbon content than to changes in the less than 2-micron clay content (figs. 18 and 19). The high arsenic level in the deeper part (6.5 to 9 cm) of core 141 is probably due to the relatively large quantity of pyrite found at this depth interval; arsenic is normally associated with pyrite.

TABLE 2—ARSENIC, ORGANIC CARBON, AND LESS THAN 2-MICRON CLAY CONCENTRATIONS IN LAKE MICHIGAN CORE AND GRAB SAMPLES

Station	Depth (cm)	Arsenic (ppm)	Organic carbon* (%)	< 2 µ clay* (%)
11	0-2	4.9	1.0	10
	2-6	9.3	1.0	36
	6-9	11	1.1	44
	9-12	6.1	0.7	20
	12-15	2.9	1.0	34
	20-23	6.4	1.0	44
	33-36	3.1	0.8	52
44	0-3	13, 12	3.0	18
	3-6	5.1	0.6	16
	6-8	7.5	0.8	19
	8-10.5	9.4	1.0	27
	10.5-13.5	4.5	1.4	27
	18.5-22	6.0	1.5	36
	33-37	7.0	1.6	40
	54-58.5	4.3	1.2	47
	84-88	5.6	1.0	50
51	0-3	25	4.6	19
	3-6	13	3.9	54
	6-10	10	3.5	41
	10-14	8.2	3.1	57
65	0-2	10	2.6	18
	2-5	4.5	1.3	14
	5-10	2.6	0.8	16
72	0-5	5.1	0.9	10
75	0-2	7.3	0.8	7
101	0-2	30	3.6	69
	2-4	20	2.3	56
	4-9	6.9	1.8	34
	33-37	7.0	1.1	31

(Continued on next page)

TABLE 2—CONTINUED

Station	Depth (cm)	Arsenic (ppm)	Organic carbon* (%)	< 2 µ clay* (%)
105	0-3	15	4.7	--
	3-6	15	2.7	72
	6-9	15	2.9	67
	26-30	3.7	1.0	81
	90-94	4.5	1.7	68
110	0-3	8.6	1.9	19
	3-6	7.2	1.3	17
	6-9	4.7	0.9	9
	9-14	3.3	0.7	13
	14-18	2.0	0.5	11
113	0-2	19	3.5	51
	2-4	14	3.3	54
	4-7	6.7	2.4	62
	30-34	4.8	1.3	65
	91-95	4.0	1.4	63
115	0-3	15	3.8	48
	3-6	8.9	3.2	43
	6-9	7.9	1.9	45
	38-44	4.4	1.7	44
118 (grab)	0-2.5	7.1	1.6	17
	2.5-7	8.5	0.8	51
118 (2" core)	0-7	7.2	0.6	54
	7-16	7.9	0.6	67
	16-20	10	0.6	56
124	0-3	18	3.6	48
	3-6	5.7	2.2	43
	6-9	5.0	2.2	55
	9-12	7.3	2.2	40
	12-15	8.3	2.7	50
	15-18	6.2	2.6	---
140	0-3	5.3, 5.4	1.2	15
	3-6	5.0, 4.3	0.4	12
	6.5-8.5	3.2, 3.1	0.8	21
	8.5-11	6.3	1.2	20
	11-14	6.1	1.6	[illegible]
	29-33	6.0	1.6	38
141	0-3.5	8.9	1.5	[illegible]
	3.5-6.5	12	1.5	27
	6.5-9	43	1.5	37
	50-54	4.4	0.8	59

(Continued on next page)

TABLE 2—CONTINUED

Station	Depth (cm)	Arsenic (ppm)	Organic carbon* (%)	< 2 μ clay (%)
142	0-4	8.1	1.6	44
	4-7	6.5	1.0	71
	7-10	6.6	0.7	69
	10-13	6.2	0.7	65
	19-23	5.9	0.3	41
	51-55	4.1	0.3	84
145	0-8	27	2.0	54
	23.7-31.6	5.4	1.5	64
	67-73.8	4.6	0.9	56
	138.3-152.3	7.5	0.9	87
	162.5-172.3	7.2	3.2	97
	229-257	5.6	0.1	92
148	96.8-120.7	5.0	0.9	48
	193.3-205.5	2.9	0.6	34
	317.7-325.8	3.0	0.3	35
150	0-3	22	4.3	46
	3-6	15	4.4	19
	6-10	14	4.0	53
	10-14	11	3.9	59
	14-20	11	3.6	65

* Organic carbon determinations were made by C. W. Beeler and L. W. Camp. Less than 2-micron clay determinations were made by W. A. White.

Arsenic concentrations in sediment-water interface samples (usually at 0 to 2 or 0 to 4 cm intervals) are plotted in figure 1 and indicate the general areas that have high arsenic accumulations. These include lake bottom areas west of Benton Harbor, Michigan (15 to 20 ppm), east of Waukegan, Illinois (13 to 27 ppm), and southwest of Grand Haven, Michigan (22 to 30 ppm). The latter area may in fact extend near enough the lake center to be continuous with either or both the other two areas. The upper layer of sediments from the extreme southwestern corner of Lake Michigan (stations 72, 75, 11, and 140) contain the lowest (about 5 to 10 ppm) concentration of arsenic observed. Conditions in these areas may be unfavorable for deposition of fine-grained sediments containing appreciable amounts of organic matter.

The general average of arsenic in the deeper sediments (> 20 cm, 25 samples) is 5.3 ± 1.9 ppm and is consistent with data published for shales (Tourtelot, 1964; Wedepohl, 1969). The average increases to 7.4 ± 3.3 ppm for intermediate layers (6 to 20 cm, 28 samples). The sediment-water interface samples (0 to 6 cm, 32 samples) average 12.4 ± 6.9 ppm arsenic.

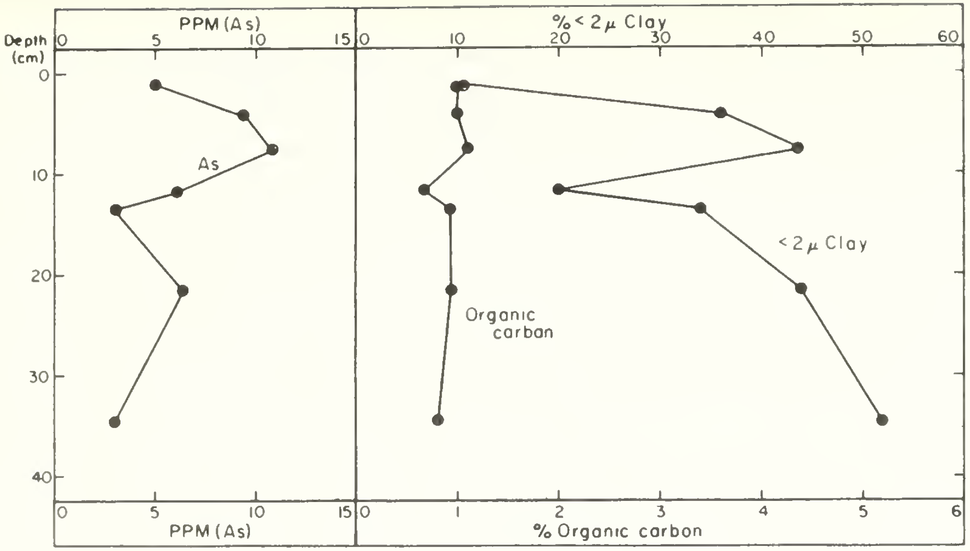


Fig. 2 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 11.

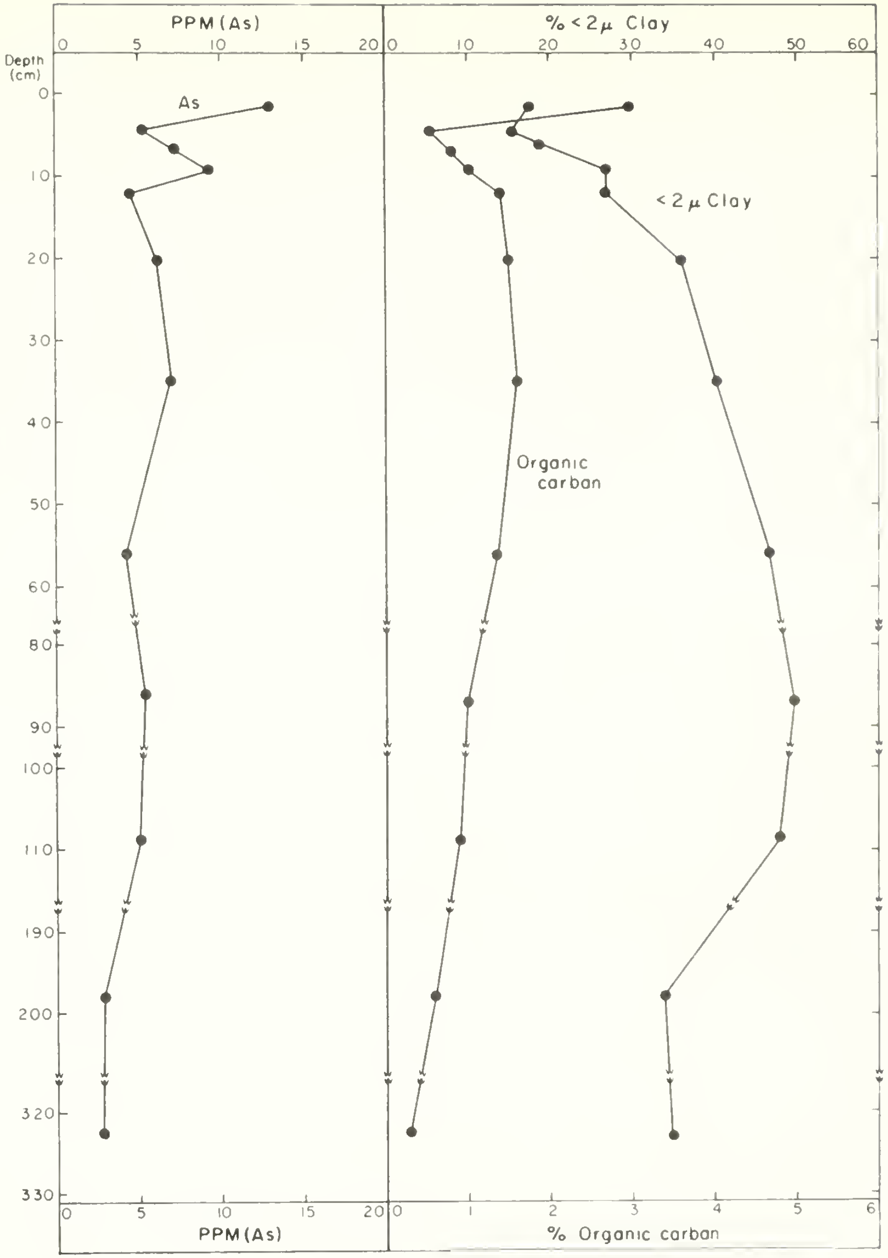


Fig. 3 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan cores 44 and 148.

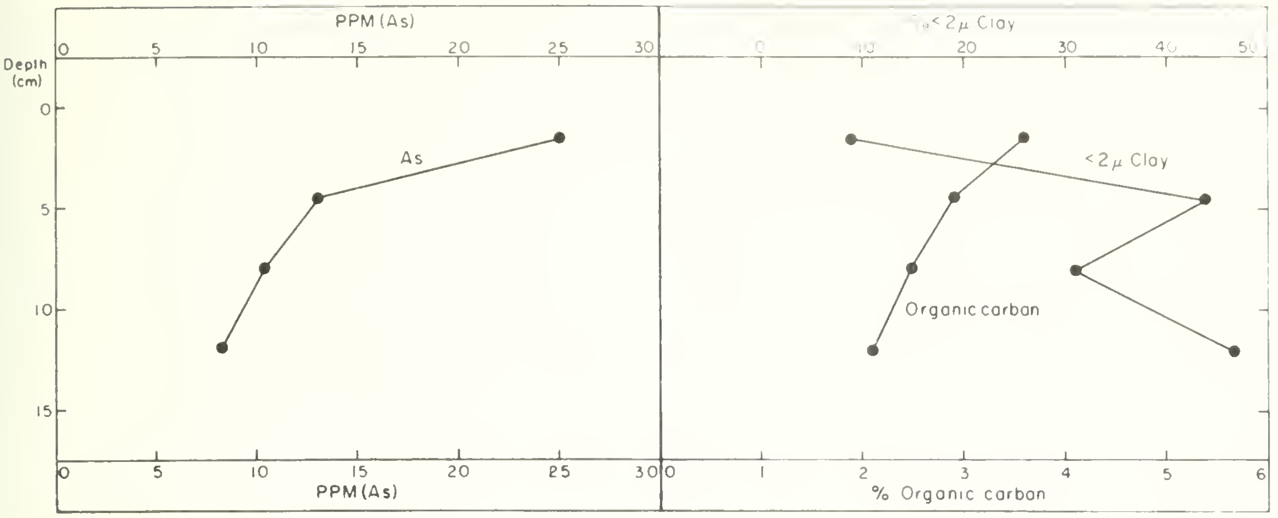


Fig. 4 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 51.

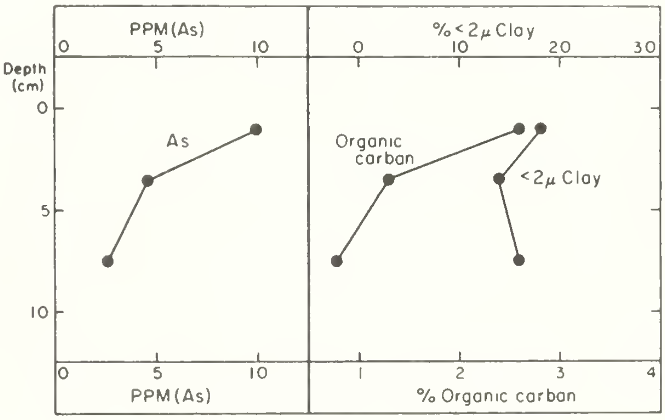


Fig. 5 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan grab sample 65.

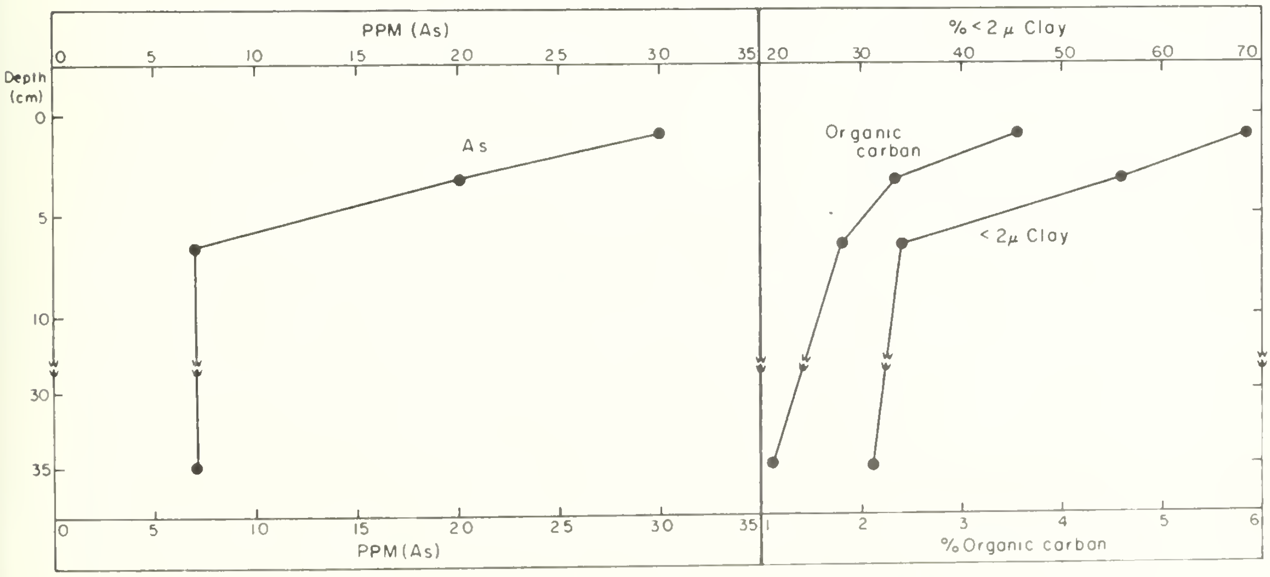


Fig. 6 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 101.

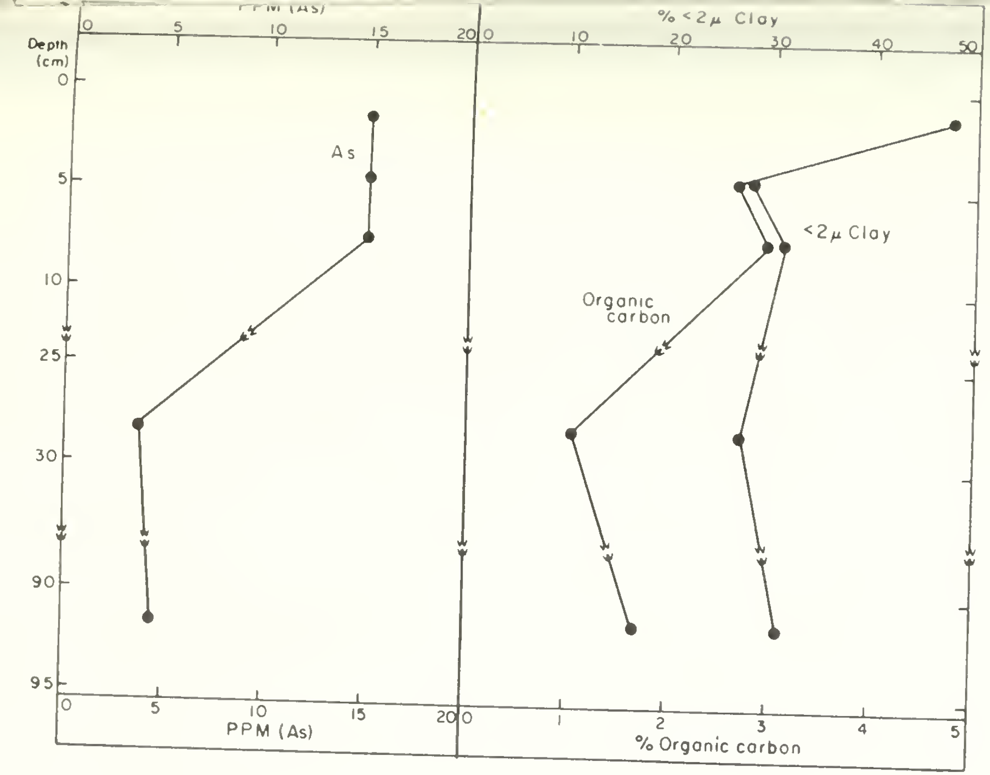


Fig. 7 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 105.

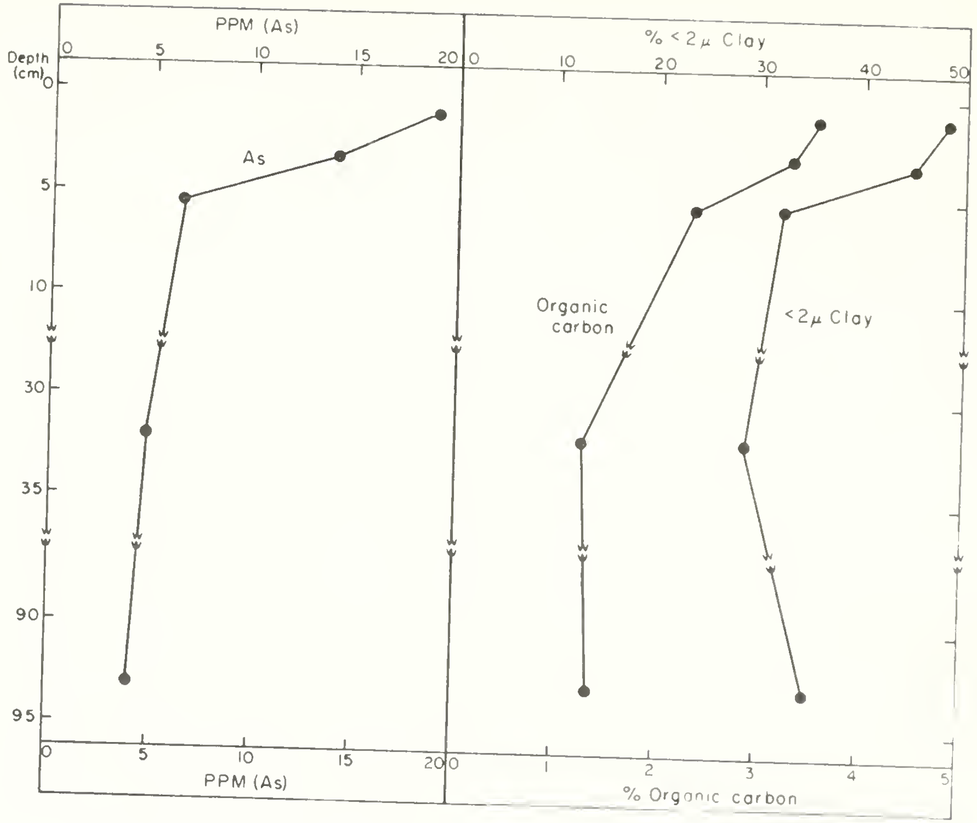


Fig. 9 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 113.

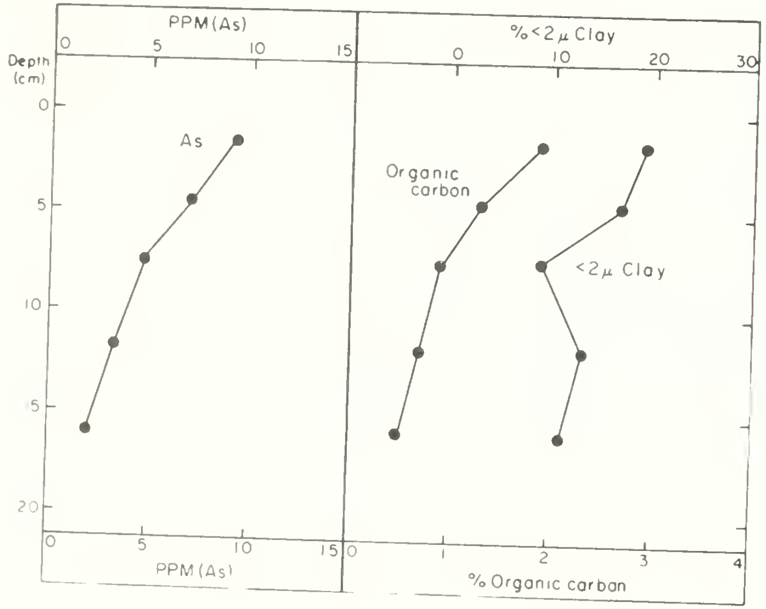
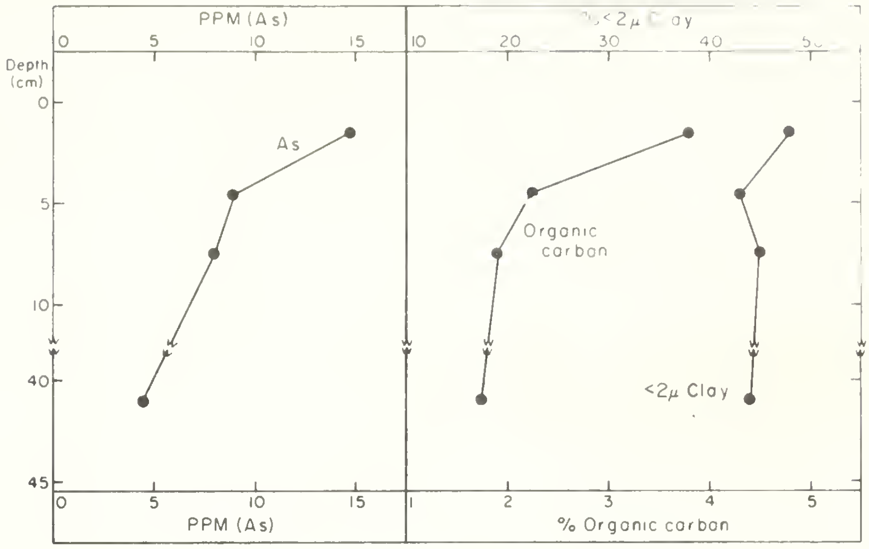


Fig. 8 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 110.

Fig. 10 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 115.



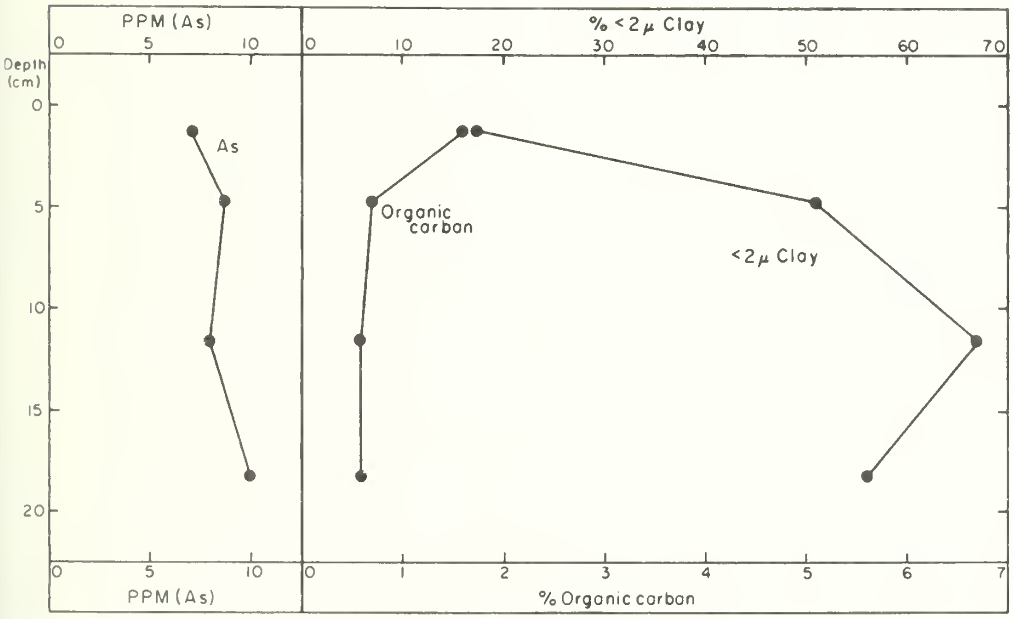
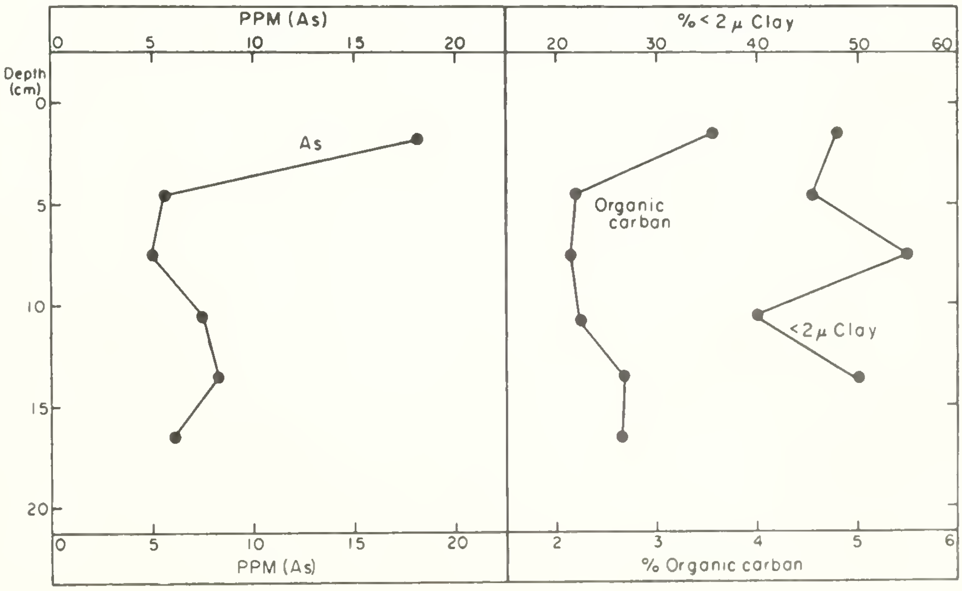


Fig. 11 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core and grab sample 118.

Fig. 12 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 124.



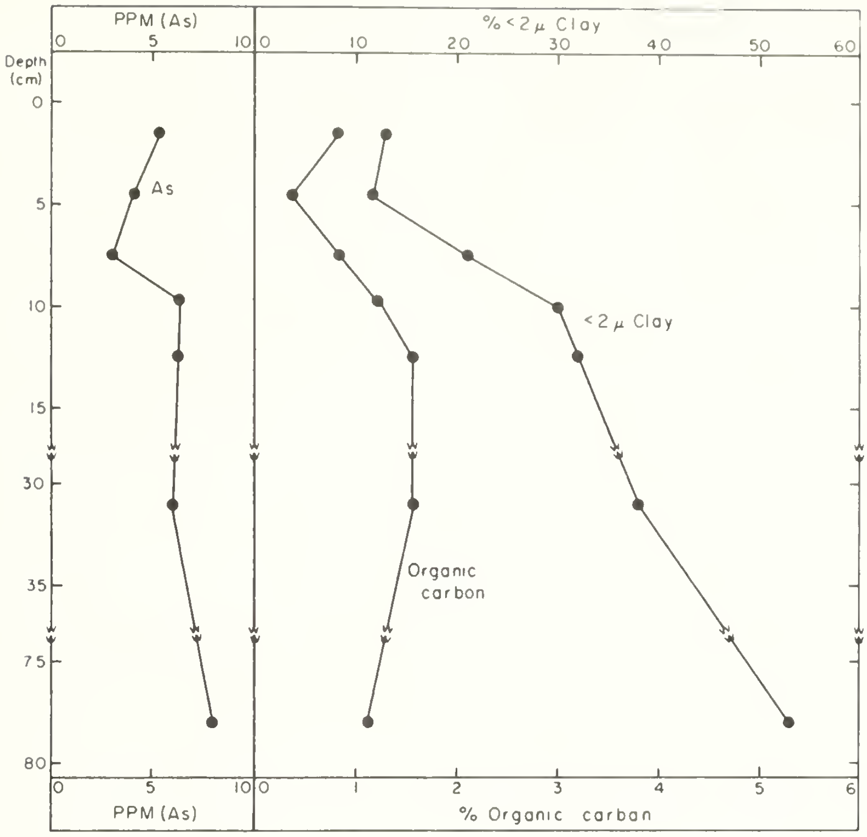


Fig. 13 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 140.

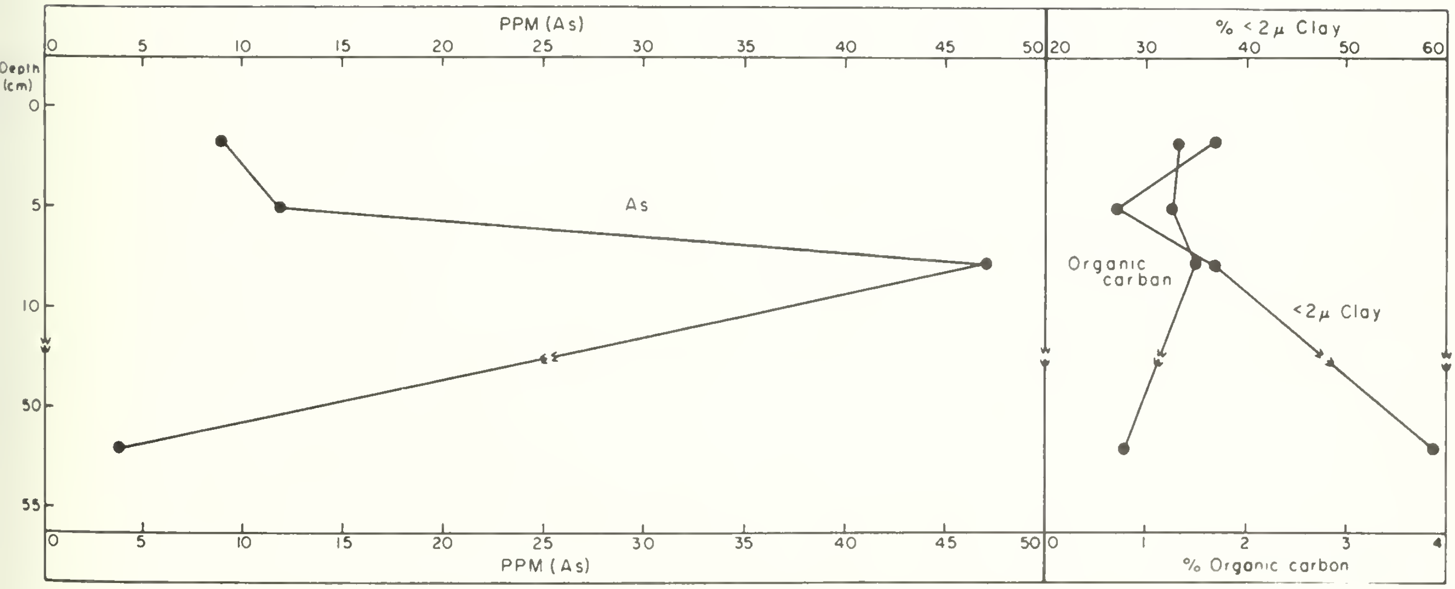


Fig. 14 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 141.

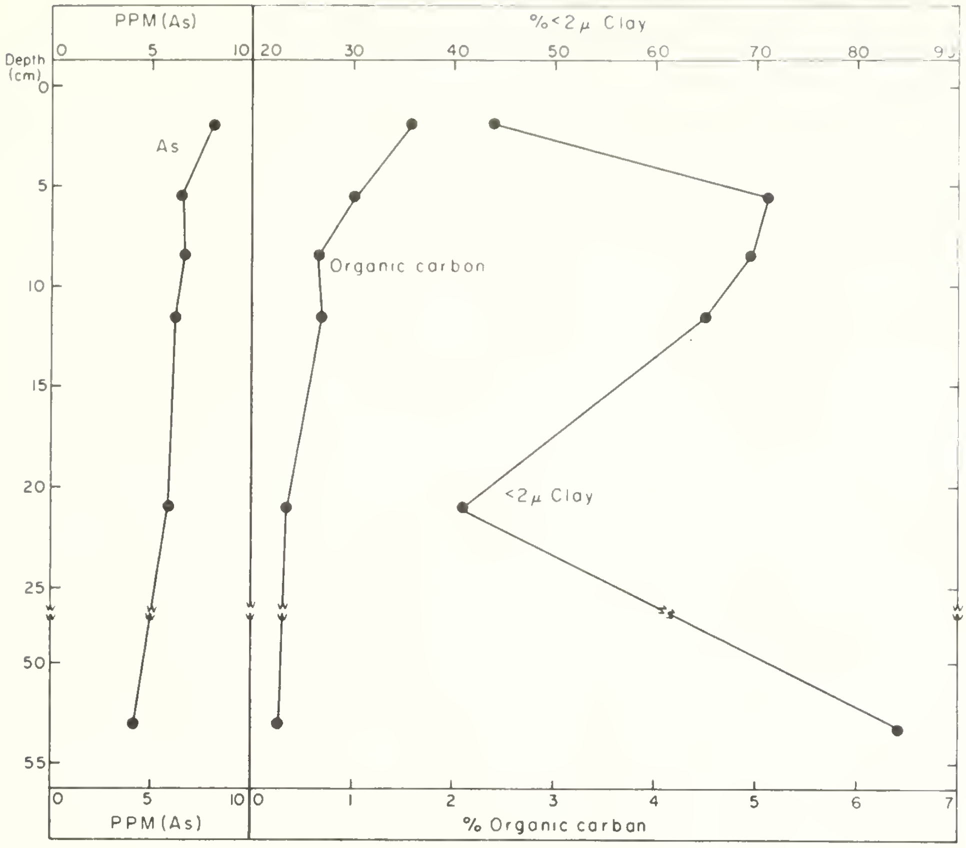


Fig. 15 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 142.

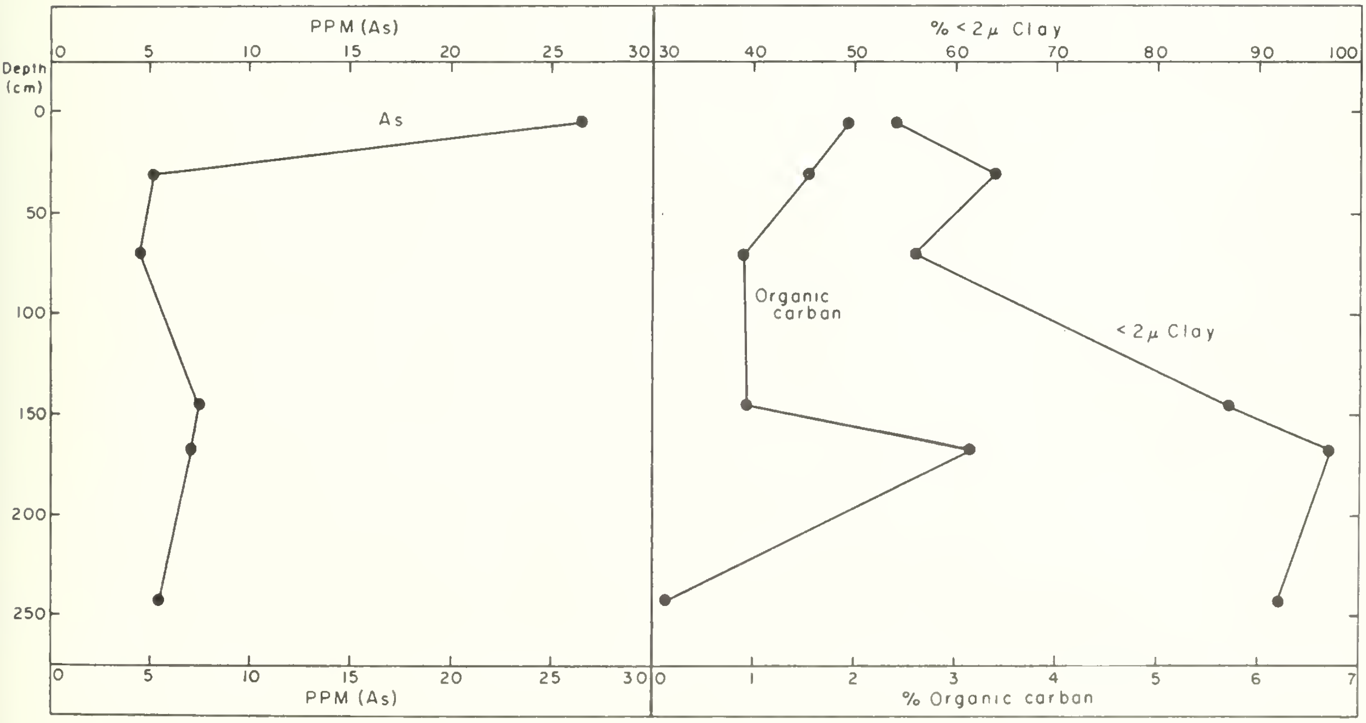


Fig. 16 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 145.

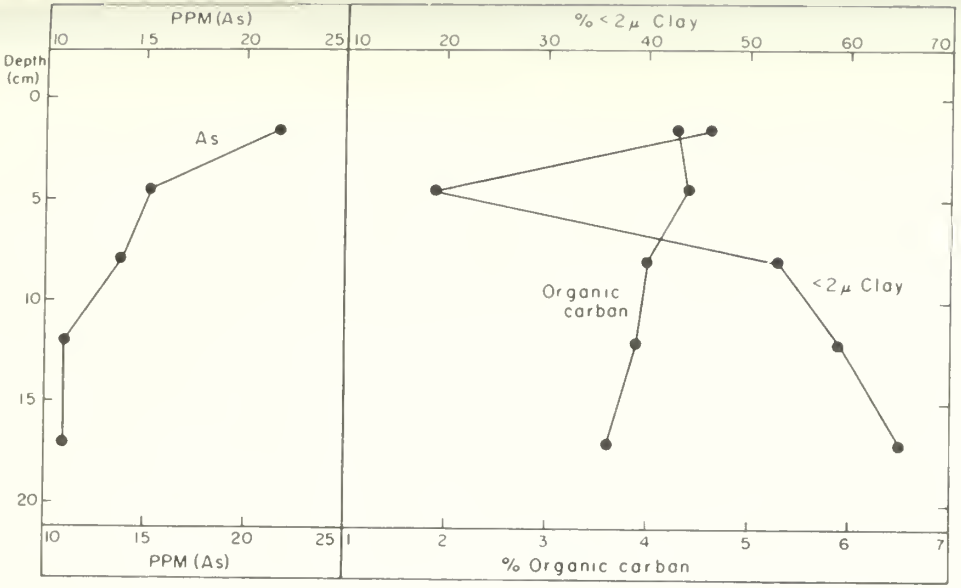


Fig. 17 - Distribution of arsenic, organic matter, and < 2 μ clay in Lake Michigan core 150.

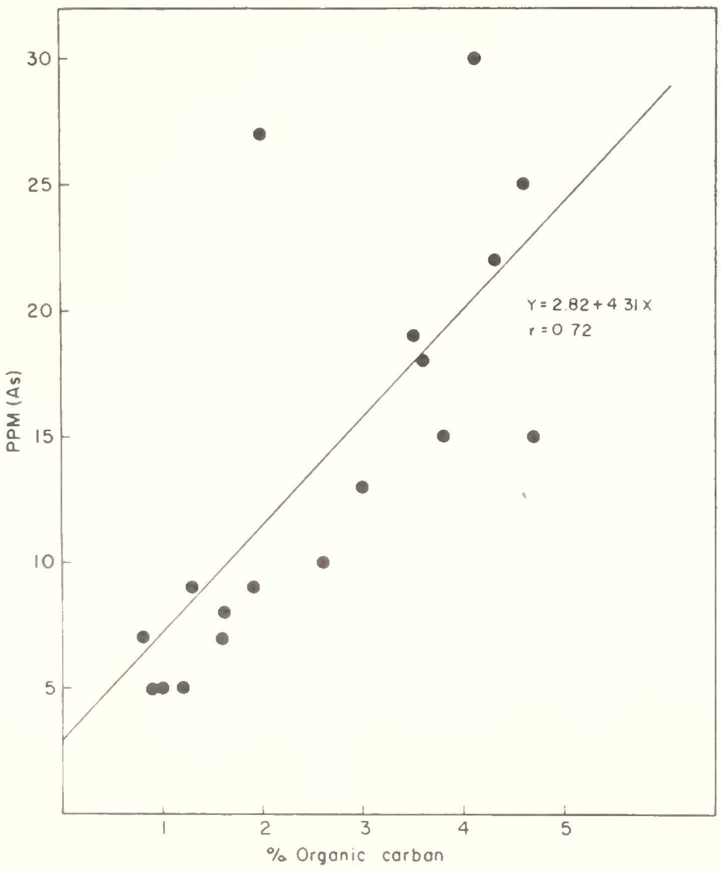


Fig. 18 - Correlation between arsenic and organic carbon contents at the sediment-water interface.

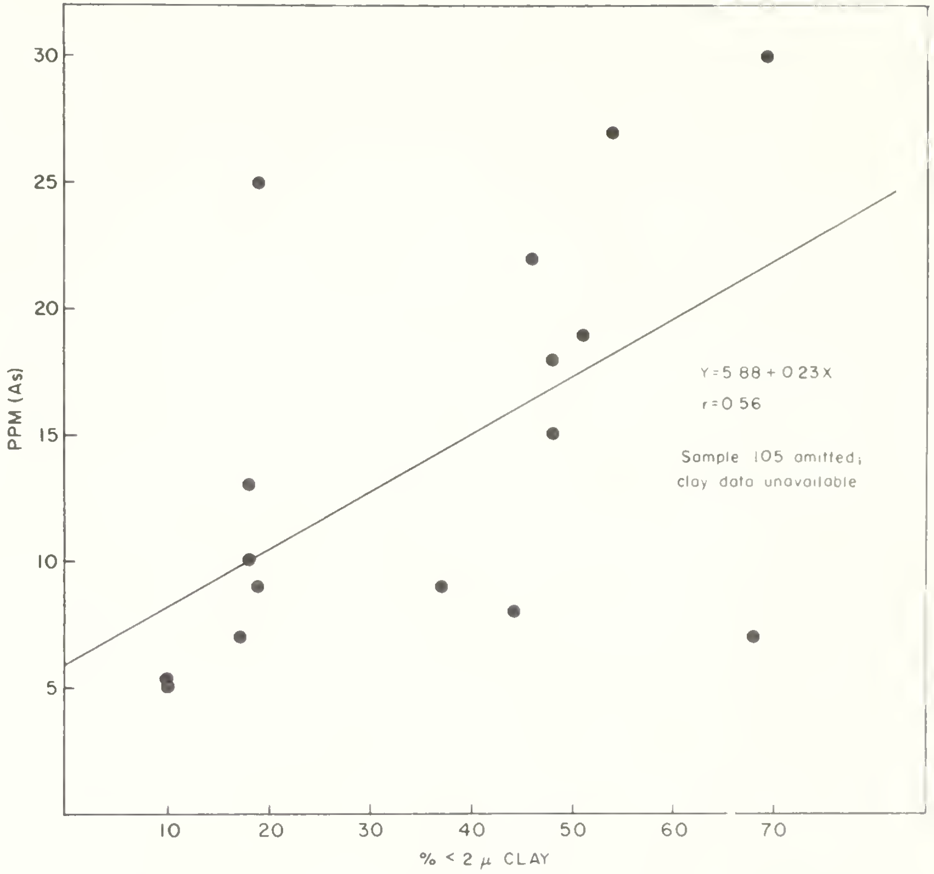


Fig. 19 - Correlation between arsenic and < 2 μ clay contents at the sediment-water interface.

SUMMARY

The accumulation of arsenic in upper, or younger, portions of southern Lake Michigan sediments is significantly related (r = 0.72) to the organic carbon content of these sediments, which, in turn, is probably related to the occurrence of fine-grained sediments in general. Data obtained for other trace constituents in southern Lake Michigan sediments (Shimp, Leland, and White, 1970; Shimp et al. [in preparation]) show trends similar to those observed for arsenic. These results indicate that arsenic has accumulated to a significant degree in the uppermost portions of many Lake Michigan sediments. Its source has not been determined, but it seems most likely that the observed accumulations are a result of man's activities in the watershed surrounding the lake.

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